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(54) Golf ball with improved cover

Golfball mit verbesselter Hülle

Revêtement amélioré pour balle de golf

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(56) References cited:
EP-A- 0 524 841 GB-A- 2 105 595
US-A- 4 919 434 US-A- 4 984 803

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Description

This invention relates to a golf ball comprising a core and a cover, the cover comprising an inner layer of a comparatively hard ionomer resin molded over the core and an outer layer of a comparatively soft material molded over the inner layer. The invention relates to a method of making a golf ball, especially the aforesaid golf ball.

5 GB 2 105 595 A describes such a golf ball with a two-layer cover. The inner layer is formed from a hard ionomer resin having a high flexural modulus, and the outer layer is formed from a soft ionomer resin having a low flexural modulus.

Golf balls which are currently available fall into two general categories -- balls which include a balata cover and balls
10 which include a more durable, cut-resistant cover. Balata covers are made from natural balata, synthetic balata, or a blend of natural and synthetic balata. Natural rubber or other elastomers may also be included. Synthetic balata is trans polyisoprene and is commonly sold under the designation TP-301 available from Kuraray Isoprene Company Ltd.

Most cut-resistant covers utilize Surlyn ionomers, which are ionic copolymers available from E.I. du Pont de Nemours & Co. Surlyn ionomers are copolymers of olefin, typically ethylene, and an alpha-beta ethylenically unsaturated carboxylic acid, such as methacrylic acid. Neutralization of a number of the acid groups is effected with metal ions, such as sodium, zinc, lithium, and magnesium. US-A-3,264,272 describes procedures for manufacturing ionic copolymers. Ionic copolymers manufactured in accordance with US-A 3,264,272 may have a flexural modulus of from about 965,25 to 6894,65 bar (14,000 to about 100,000 psi) as measured in accordance with ASTM method D-790. US-A-4,690,981 describes ionic copolymers which include a softening comonomer. Ionic copolymers produced in accordance with US-A 4,690,981 are considered "soft" ionic copolymers and have a flexural modulus of about 2800 to about 8500 psi.

Other cut-resistant materials which can be used in golf ball covers are ionic copolymers available from Exxon under the name lotek, which are similar to Surlyn ionic copolymers except that acrylic acid is used rather than methacrylic acid.

25 A number of golfers, primarily professional and low handicap golfers, prefer balata covered balls because of the higher spin rate, control, "feel," and "click" which balata provides. "Feel" is the overall sensation imparted to a golfer when the ball is hit, and "click" refers to the sound made when the clubhead hits the ball. However, balata covered balls are more expensive and are less resistant to cutting than Surlyn covered balls.

Conventional balata covered 3 piece golf balls are produced by winding resilient, low heat-resistant elastic thread
30 over a soft rubber or liquid rubber center, which must first be frozen to permit winding the rubber thread, and molding a conventional soft balata cover over the windings. The balata is conventionally vulcanised or crosslinked by using sulfur as the crosslinker or vulcanizing agent.

This process has proven to be very costly and requires numerous extra production steps in manufacture, extended cure time frames in hot room areas, and specified ambient conditions in order to complete the sulfur crosslinking system.
35 The procedures limit the consistency of the crosslinking, reduce the ability to initiate good work-in-process production procedures and maintain normal inventory levels, and limit the time frame after ball finishing for final cover crosslinking which develops the final physical properties of the cover and the ball.

In addition, conventional processing methods for balata covered balls produce relatively low yields of good cosmetic quality balls because the additional processing steps which are required before complete cover crosslinking
40 occurs can damage the cover surface. Also, extra steps are required in conventional balata ball production methods including chlorination and ball rinses to prepare the cover surface for acceptable paint adhesion to the balata surface. Multiple coats of pigmented paint are normally applied prior to logo stamping, then a final clear, two component or ultra violet curable coating is applied to protect the ball surface and logo.

While the ball is played, additional paint durability problems may be exhibited in the form of scuffing and micro
45 cracking. Balata golf balls produced using the conventional process methods also suffer from color and color stability problems.

Surlyn covered balls are cheaper than balata balls not only because Surlyn is cheaper than balata but because the Surlyn balls can be processed after molding much easier and faster than balata balls. The substantial processing differences between balata balls and Surlyn balls can be seen by comparing Tables 1 and 2, which describe the conventional processing steps for manufacturing 3 piece balata and 3 piece Surlyn golf balls. The term "3 piece" is commonly used to refer to a golf ball which has a center, a layer of elastic windings over the center, and a cover. The term "2 piece"
50 is used to refer to a golf ball which has a solid core and a cover. Table 3 describes the conventional processing steps for a 2 piece Surlyn golf ball. The processing steps described in Tables 1-3 are well known in the golf ball industry, and a detailed description thereof is unnecessary.

Table 1

Conventional 3 Piece Balata Process	
5	1. center rubber compound mixed
10	2. mill and preform pellets
15	3. mold center
20	4. center flash removed
25	5. freeze center
30	6. wind core (conventional elastic thread)
35	7. compression mold heated preform pellets into single halfshells
40	8. place halfshells over wound core
45	9. compression mold balata balls
50	Note: cover is only partially crosslinked after this molding step.
55	10. freeze molded ball prior to buffing
60	11. remove balls and transfer to fiberglass bags
65	12. transport frozen balls to holding freezer
70	13. seam buff ball being careful not to buff seam too deep because of the soft cover
75	14. grade balls after seam buff for quality level
80	15. cure balata ball cover in alcohol/RR2 crystals solution, (7 hours soak)
85	16. remove balls from solution and water rinse
90	17. transport balls into hot room to cure for 7 days
95	18. before removing balls from room use benzene test method to insure proper cover cure
100	19. remove balls from cure room and soak in acetone, (hazard solvent disposal necessary)
105	20. remove balls from acetone and allow to air dry
110	21. chlorination process using hydrochloric acid and sodium hypochlorite; load balls into solution tank (must be done in an exhausted area for safety), (chlorination solution must be neutralized before discharge into city sewer drain)
115	22. remove balls and rinse in clear water tank, up and down motion
120	23. remove and repeat in second tank
125	24. remove and repeat in third tank
130	25. remove and rinse in acetone tank
135	26. apply primer
140	27. apply 1st top coat
145	28. pad print logo
150	29. apply clear top coat
155	30. inspect and package

Table 2

Conventional 3 Piece Surlyn Process	
5	1. center rubber compound mixed
10	2. mill and preform slug
15	3. mold center
20	4. center flash removed
25	5. wind center (conventional elastic thread)
30	6. injection mold halfshells
35	7. place halfshells over core
40	8. compression mold ball
45	9. seam buff parting line
50	10. vibratory finish ball
55	11. apply primer
60	12. pad print logo
65	13. apply clear top coat
70	14. inspect and package

Table 3

Conventional 2 Piece Surlyn Process	
30	1. core rubber compound mixed
35	2. mill and preform slug
40	3. mold core
45	4. centerless grind core to size
50	5. injection mold Surlyn cover around core
55	6. seam buff parting line
60	7. vibratory finish ball
65	8. apply primer
70	9. pad print logo
75	10. apply clear top coat
80	11. inspect and package

The balata cover is not fully cured and crosslinked until the 7 day cure step of step No. 17 in Table 1 is completed. As a result, the partially cured balata balls require more careful handling and additional process steps than the Surlyn balls. For example, after the balata balls are removed from the mold they must be frozen before the parting line seam on each ball is buffed. Also, because the balata covers are softer, they must be examined more carefully for defects which could be caused by the processing steps.

As stated previously, balata covers are generally vulcanized or cured using sulfur as the vulcanizing agent. Sulfur is included in the cover composition in an amount of about 1 to 2% by weight of the balata. The vulcanizing occurs during the final molding operation in which two hemispherical halfshells of the cover are molded over the thread-wound core in a compression mold. However, the molding temperature and time is limited by the threads, which can be dam-

aged by high heat. Accordingly, the cover is not fully cured when it is removed from the mold and requires the exposure as described in Tabl 1, step 15 to accelerate the cure through migration of the RR2 crystals accelerator material into the cover cross sectional area to complete the vulcanization of the cover. RR2 crystals are the reaction product of 1,1 methylene dipiperidine and carbon disulfide and are available from Rockland React-Rite, Inc. of Rockmart, Georgia. 5 RR2 crystals are dissolved in isopropyl alcohol solvent in the amount of about 10% by weight of crystals to about 90% by weight of alcohol.

By way of example, one specific commercial balata covered ball which was sold by Wilson Sporting Goods Co. had the cover composition described in Table 4.

10

Table 4

Prior Art Balata Cover Composition (Parts by Weight)	
15	Trans Polyisoprene 84.00
	Natural Rubber or Polyisoprene 16.00
20	ZnO 13.00
	TiO ₂ 17.00
25	Blue Toner 0.20
	Stearic Acid 0.26
	Thiozole Accelerator 0.26
	Sulfur 1.20
	Total 131.92

30

This system was not completely crosslinked until steps 15 through 17 were performed in Table 1.

The Zinc Oxide was used as a filler and a gravity adjuster. The blue toner was used to enhance the white color and was Ultramarine Blue from Whittaker, Clark & Daniels, Inc. of South Plainfield, New Jersey.

35

Two piece or solid golf balls conventionally include a core which includes a thermally crosslinkable elastomer such as polybutadiene. The polybutadiene is cured or crosslinked by including in the core composition a crosslinking agent and a crosslinking initiator. Common crosslinking agents are zinc salts of monocarboxylic acids such as zinc diacrylate, zinc acrylate, and zinc methacrylate. The crosslinking initiator provides free radicals, and common crosslinking initiators are organic peroxides such as dicumyl peroxide.

40

US-A 3,784,209, 4,065,537, 4,266,772, 4,483,537, 4,683,257, 4,688,801, 4,714,253, and 4,715,607 describe various solid cores for golf balls which include elastomers such as polybutadiene which are cured or crosslinked by zinc diacrylate and peroxide or similar ingredients.

US-A 4,792,141 and 4,931,376 describe golf ball covers which include blends of balata and elastomers such as polybutadiene and trans polyoctenylene rubber. However, the rubber compositions are cured by the conventional sulfur curing technique.

45

US-A 4,884,814 describes a golf ball cover which is formed from a blend of "hard Surlyn" and "soft Surlyn". The hard Surlyn is described as a high modulus ionomer having a flexural modulus of from about 2068,39 bar to 3792,06 bar (30,000 to 55,000 psi) as measured in accordance with A.S.T.M. Method D-790. The soft Surlyn is described as a low modulus ionomer having a flexural modulus of from about 206,84 bar to 482,63 bar (3000 to about 7,000 psi).

The invention provides a golf ball which has many of the desirable features of balata covered balls but is more durable, more cut-resistant, and easier and less expensive to manufacture than conventional balata covered balls.

50

A golf ball cover in accordance with the invention includes an inner layer formed from a relatively hard, cut-resistant material such as ionomer resin and an outer layer of soft material such as balata or a blend of balata and other elastomers. Preferably, the outer layer is a blend of balata and a thermally crosslinkable elastomer such as polybutadiene. The balata and elastomer are crosslinked during the molding of the ball by a crosslinker such as zinc diacrylate and a crosslinking initiator such as organic peroxide rather than using the conventional sulfur and RR2 crystals curing system for balata covers. The outer layer of the cover is completely crosslinked when the ball is removed from the mold, and subsequent processing steps can be performed in the same manner as on Surlyn covered balls. The inner layer of the cover provides good cut resistance, and the outer layer provides the sound, feel, and spin characteristics of a balata cover. The cover can be used in either 2 piece or 3 piece balls.

Fig. 1 is a cross section of a two piece ball formed in accordance with the invention;
 Fig. 2 is a cross section of a three piece ball formed in accordance with the invention; and
 Fig. 3 and 4 are rheology charts showing curing comparisons of various balata covers.

5 The cover of the invention is formed from two layers -an inner layer which is molded over a solid or a wound core and an outer layer which is molded over the inner layer. The inner layer is formed from a relatively hard, cut-resistant material such as ionomer resin, and the outer layer is formed from relatively soft material such as elastomeric or polymeric material selected from the class consisting of natural balata, synthetic balata, natural rubber, polybutadiene, and polyoctenylene rubber. Polyoctenylene rubber having a high trans content is available under the trade name Vestenamer from Huls Corp. of West Germany. Particular grades of Vestenamer which are suitable are Vestenamer 8012 and
 10 Vestenamer 6213.

The ionomers used for the inner layer are available from E. I. du Pont de Nemours & Co. under the name Surlyn and from Exxon under the name Iotek. Surlyn resins are described in US-A-3,264,272. As described in that patent, various metal ions can be used to neutralize the acid groups, including sodium, zinc, lithium, and magnesium. The ionomer resins generally fall into three categories which are characterized by hardness or stiffness -- standard, high modulus, and low modulus. The standard resins have a flexural modulus in the range of about 2068,39 bar to 3792,06 bar (30,000 to about 55,000 psi) as measured by ASTM Method D-790. (Standard resins are referred to as "hard Surlyns" in US-A-4,884,814.) The high modulus resins have a flexural modulus in the range of about 3792,06 bar to 6894,65 bar (55,000 to about 100,000 psi). The low modulus resins have a flexural modulus in the range of about 193,05 bar to 586,05 bar (2800 to about 8500 psi).

20 Specific standard Surlyn resins which can be used in the inner layer include 8940 (sodium), 9910 (zinc), 7930 (lithium). Specific standard Iotek resins which can be used include 8000 (sodium), 8020 (sodium), 8030 (sodium), 4000 (zinc), and 4010 (zinc).

Low modulus ionomers are described US-A-4,690,981 and include a softening comonomer. Specific low modulus Surlyns which can be used in the inner layer include 8120 (sodium), 8320 (sodium), and 9320 (zinc).

25 Specific high modulus Surlyns which can be used in the inner layer include 8220 (sodium), 8240 (sodium), 9220 (zinc), and AD-8181 (lithium).

The ionomer resins can be used alone or in blends of two or more types of ionomers, for example, blends of sodium/zinc ionomers, sodium/lithium ionomers, zinc/lithium ionomers, and sodium/zinc/lithium ionomers. Blends of ionomers of different stiffness can also be used, for example, blends of standard/high modulus ionomers, standard/low modulus ionomers, low/high modulus ionomers, and low/standard/high modulus ionomers.

30 The relatively soft elastomeric material of the outer layer has a flexural modulus in the range of about 1378,93 bar to 1723,66 bar (20,000 to 25,000 psi), and in one specific embodiment had a flexural modulus of from 1528,20 bar to 1542,95 bar (22,165 to 22,379 psi).

35 The outer layer preferably comprises a blend of balata and one or more thermally crosslinkable elastomeric polymers. The balata can be either natural or synthetic balata or a blend of both. The thermally crosslinkable elastomers can be those which have heretofore been used in core compositions of golf balls, for example, as described in US-A-3,784,209, 4,065,537, 4,266,772, 4,483,537, 4,683,257, 4,688,801, 4,714,253, and 4,715,607.

As described in those patents, suitable crosslinkable elastomers include homopolymers, copolymers or terpolymers of butadiene, isoprene or chloroprene. Preferably, the elastomer is 1,4 polybutadiene having a cis structure in a proportion of at least 40%. Most preferably the polybutadiene rubber contains at least 90% and even more preferably at least 95% of cis-1,4 bonds. If desired, natural rubbers, polyisoprene rubbers, styrene/butadiene rubbers, or the like may be blended with the polybutadiene rubber. Another suitable elastomer is polyoctenylene rubber having a high trans content.

45 The crosslinking agent can be one or more metallic salts of unsaturated fatty acids or monocarboxylic acids, particularly, zinc, calcium or magnesium salts of acrylic acid and methacrylic acid. Zinc diacrylate, zinc acrylate, and zinc methacrylate are particularly suitable.

Any of a number of known crosslinking initiators can be used. These initiators supply free radicals and include various organic peroxides such as dicumyl peroxide and n-Butyl-4, 4-bis (t-butylperoxy) valerate on calcium silicate, which is available from R. T. Vanderbilt, Inc. of Norwalk, Connecticut under the trademark Varox 230XL. Suitable crosslinking agents and crosslinking initiators are described in the aforementioned patents which describe polybutadiene cores.

50 The balata is preferably present in an amount ranging from 25% to 99% of the total polymer content of the outer layer of the cover. The balance of the polymer content, namely from 75% to 1% of the total polymer content, is preferably provided by polybutadiene having a high cis-1,4 content, but other suitable crosslinkable elastomers such as natural rubber, Vestenamer, etc. can be blended with the polybutadiene as desired.

55 The amount of the crosslinking agent generally ranges from 20 to 50 parts by weight of the total polymer content of the outer layer, and is preferably about 35 to 45 parts by weight.

The amount of the crosslinker initiator can range from about 3/4 to 3-1/2 parts by weight of the total polymer content of the outer layer, and preferably is about 2 to 2-1/2 parts by weight.

Any suitable filler, for example zinc oxide, can be added to both the inner and outer layers of the cover. Zinc oxide not only acts as a filler and as a gravity adjuster but may also provide crosslinking. Other conventional ingredients may also be included, such as titanium dioxide and Ultramarine Blue.

Fig. 1 illustrates a two-piece golf ball 10 which includes a solid core 11 and a cover 12 which comprises a relatively hard inner layer 13 of one or more ionomer resins and a relatively soft outer layer 14 of polymeric material. The solid core 11 can be formed in the conventional manner.

Fig. 2 illustrates a three-piece golf ball 16 which includes a wound core 17 which comprises a center 18 and a layer 19 of windings of elastic thread. The center 18 may be solid or a liquid filled balloon. Such wound cores 17 are also conventional. A cover 20 includes a relatively hard inner layer 21 of one or more ionomer resins as previously described and a relatively soft outer layer 22 of polymeric material as previously described.

The diameter of the core 11, 17 of either the two-piece or the three-piece ball 10 or 16 can be within the range of about 25,40 mm to 38,10 mm (1.000 to 1.500 inch). The thickness of the inner layer 13, 21 can be within the range of about 0,635 mm to 7,30 mm (0.0250 to 0.2875 inch) to provide a total diameter of the inner layer 13, 21 and core 11, 17 within the range of about 39,37 mm to 40,386 mm (1.550 to 1.590 inch). The thickness of the outer layer 14, 22 can be within the range of about 1,143 mm to 16,51 mm (0.0450 to 0.0650 inch) to provide a total ball diameter of 42,67 mm (1.680 inch). The preferred dimensions are a core 11, 17 diameter of 38,1 mm (1.500 inch), an inner layer 13, 21 thickness of 0,9398 mm (0.037 inch) - inner layer 13, 21 diameter of 40,01 mm (1.575 inch) - and an outer layer thickness of 0.0525 inch (total ball diameter of 1.680 inch or 42,67 mm).

20 Example I

Two specific solid core compositions used with the new two-layer cover had the composition described in Table 1. One core was used in a golf ball which was designated as a 90 compression ball, and the other core was used in a golf ball which was designated as a 100 compression ball.

25

Table 5

Composition of Core (Parts by Weight)		
	90 Compression	100 Compression
Polybutadiene Rubber	95.00	95.00
Vestenamer 8012	5.00	5.00
Zinc Oxide	12.20	11.10
Zinc DiAcrylate	35.00	38.00
Antioxidant	0.80	0.80
Peroxide (Luperco 101 XL)	0.80	0.80
Liquid Monomer SR-351 (TMPTA)	5.00	5.00
Total	153.80	156.80

45 The antioxidant was 2,2'-Methylenebis (4-methyl-6-tert-butylphenol) which was obtained from R. T. Vanderbilt Co. of Norwalk, Connecticut under the trade name Vanox MBPC.

The peroxide is an organic peroxide available from Atochem North America Inc., Philadelphia, Pennsylvania.

The Liquid Monomer is Trimethylolpropane Triacrylate available from Sartomer, Westchester, Pennsylvania.

The core was processed according to the conventional steps:

50

1. core rubber compound mixed
2. mill and preform slug
3. mold core
4. centerless grind core to size.

55

The composition of the inner layer of the cover is described in Table 6.

Table 6

Composition of Inner Layer of Cover (Parts by Weight)	
Ionomer Type	Blend Ratio
Sodium - Surlyn 8940	75%
Zinc - Surlyn 9910	25%

5

10

The inner layer can be molded in one of two methods:

- 15 1. Injection molded over the core in a manner which is conventionally used to injection mold ionomers over a solid core.
 2. Injection mold halfshells, place halfshells over the core, compression mold the inner cover over the core.

20 After either method of molding the inner layer is completed, the surface is centerless ground to a preferred size of 1.575 inch in diameter prior to the final cover molding step.

The composition of the outer layer of the cover is described in Table 7.

Table 7

Composition of Outer Layer (Parts by Weight)	
Trans Polysoprene (TP-301)	60.00
Polybutadiene	40.00
Zinc Oxide	5.00
Titanium DiOxide	17.00
Ultramarine Blue color	.50
Zinc DiAcrylate	35.00
Peroxide (Varox 230 XL)	2.50
Total	160.00

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Ultramarine Blue is a blue toner which is used to enhance the white color of the cover and is available from Whitaker, Clark & Daniels, Inc. of South Plainfield, New Jersey.

The outer layer of the cover was made by conventional mixing and molding procedures. The components of the composition are mixed on a mill such as a two roll mill to form slabs. Slabs are fed into a dicer which cubes the cover compound prior to the injection molding to form generally hemispherical halfshells. The halfshells are placed about the inner layer of the ball in a compression molding machine which fuses the halfshells to each other and to the inner layer. The compression molding operation is carried out under a temperature of about 121,11°C to 176,67°C (250 to 350°F) for about 5 to 10 minutes. The molding temperature causes the elastomer to crosslink, and it is believed that the ball is fully crosslinked when it is removed from the compression mold.

50 The outer layer composition can also be used in a conventional injection molding machine to form an injection molded outer layer about the inner layer.

The rheology chart of Fig. 3 shows that the crosslinking agent causes crosslinking of not only the polybutadiene but also of the balata and that the composition is fully crosslinked after the molding operation. The rheology chart was prepared by tests conducted on a Monsanto Moving Die Rheometer MDR 2000 available from Monsanto Instruments & Equipment of Akron, Ohio. The rheometer is used to measure cure characteristics of rubber and measures the reaction torque as a function of cure time or degree of vulcanization. Curing was performed at 300° F or 148,89°C.

Figure 3 compares the following outer layer compositions.

EXG24-60: from Table 4

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- EXG24-71: same as EXG24-60 but without polybutadiene (100% TP301)
 EXG24-58: same as EXG24-60 but without polybutadiene and peroxide

5

Table 8

	EXG24-60
10	Trans-Polyisoprene TP-301 84.00
	Polybutadiene 16.00
	ZnO 13.00
15	ZDA 35.00
	TiO2 17.00
	Ultramarine Blue .50
	Peroxide (Varox 230XL) 2.50
20	Total 168.00

EXG24-58 without peroxide exhibits very poor curing characteristics. The other two formulas have comparable
 25 curves, which indicate that the composition which includes balata and polybutadiene is just as crosslinkable as the composition which contains only balata and no polybutadiene.

Figure 4 is a rheology chart which compares the three outer layer compositions set forth in Table 9:

30

Table 9

	EXG24-78	EXG24-77	EXG24-76
35	Trans Polyisoprene 84.00	84.00	84.00
	Natural Rubber 16.00	16.00	16.00
	ZnO 13.00	13.00	13.00
	TiO 2 17.00	17.00	17.00
40	Ultramarine Blue .20	.20	.20
	Stearic Acid .26	.26	.26
	Thiozale Accelerator .26	.26	.26
	Sulfur 1.20	1.20	---
45	RR-2 Crystals 1.50	---	---
	Total 133.42	131.92	130.72

Formula EXG24-78 is comparable to a conventional prior art balata cover which is cured by sulfur and the step of
 50 soaking the completed ball in an alcohol/RR2 crystal solution described in Step No. 15 of Table 1. However, in order to test the composition on the MDR 2000 Rheometer the RR2 crystals were incorporated into the composition to simulate the subsequent soaking step.

Formula EXG24-77 is the same as formula EXG24-78 but omits the RR2 crystals. Formula EXG24-76 is the same as formula EXG24-78 but omits both sulfur and the RR2 crystals.

55 It is significant to note the difference between the cure rheology of the balata compositions illustrated in Figure 4 and the new balata compositions cured by Zinc diacrylate and peroxide illustrated in Figure 3. The rheology physical properties for the compositions in Figure 4 are so low compared to the compositions of Figure 3 that the scale of Figure 4 had to be changed from 0 to 100 torque units to 0 to 5 torque units in order to be meaningful. The cover composition of formula EXG24-60 of Figure 3 has significantly higher torque than formula EXG24-78 of Figure 4. Also, the rheology

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cure curve for formula EXG24-78 shows reversion, while the cure curve of formula EXG24-60 shows essentially a curve which is flatlined.

Because the balata-containing outer layer of the cover in accordance with the invention is fully crosslinked after the molding operation, the golf balls can be processed in a manner in which is very similar to the processing of Surlyn covered balls, thereby greatly facilitating the additional processing steps and reducing the overall cost of the balls. The processing steps for 3 piece and 2 piece balls formed in accordance with the invention are described in Tables 10 and 11, and these processing steps can be compared with the steps described in Tables 1-3.

Table 10

New 3 Piece Process	
10	1. center rubber compound mixed
15	2. mill and preform slug
20	3. mold center
25	4. center flash removed
30	5. wind center with heat resistant thread
35	6. injection mold halfshells for the inner layer of the cover
40	7. place the halfshells of the inner layer over the core
45	8. compression mold the halfshells of the inner layer over the core
50	9. grind inner cover surface to size if required
55	10. injection mold the halfshells of the outer layer
60	11. place the halfshells of the outer layer over the molded inner layer
65	12. compression mold ball
70	13. seam buff parting line
75	14. vibratory finish ball
80	15. apply primer
85	16. logo print
90	17. apply clear top coat
95	18. inspect and package

Table 11

New 2 Piece Process		
5	1.	core rubber compound mixed
	2.	mill and preform slug
	3.	mold core
10	4.	centerless grind core to size
	5.	injection mold Surlyn inner layer of the cover around core or injection mold halfshells for the inner cover layer then compression mold halfshells around core
	6.	grind inner cover surface to size if required
15	7.	injection mold halfshells of the outer layer of the cover
	8.	place halfshells of the outer layer over the molded inner layer
	9.	compression mold the halfshells of the outer layer over the inner layer
20	10.	seam buff parting line
	11.	vibratory finish ball
	12.	apply primer
	13.	logo print
25	14.	apply clear coat
	15.	audit inspect and package
30	Note: The outer layer of the cover can also be injection molded over the inner layer using conventional injection molding technology.	

Steps 5 and 10 through 25 in Table 1 have been eliminated using the new technology described in Tables 10 and 11. The 30 steps used to process balata covers in the old procedure have been replaced by 18 steps for 3 piece balls and 15 steps for 2 piece balls.

Balls formed in accordance with Example 1 (100 compression) were flight tested with an automatic hitting machine using a driver, a 5 iron, and a pitching wedge. The inventive balls were compared with Titleist Tour 100 balata balls, which is a popular balata-covered 3 piece ball. The comparative flight test data is found in Table 12.

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Table 12

HARD DRIVER - 7 Degree Launch Angle				
	Carry	Difference	Total	Difference
Titleist Tour 100 Balata	251.0	Base	268.7	Base
Example 1 ball	252.3	+ 1.3	272.2	+ 3.5
HARD DRIVER - 9 Degree Launch Angle				
Titleist Tour 100 Balata	250.5	Base	258.7	Base
Example 1 ball	254.0	+ 3.5	263.7	+ 7.6
HARD DRIVER - 11 Degree Launch Angle				
Titleist Tour 100 Balata	249.6	Base	255.0	Base
Example 1 ball	255.0	+ 5.3	262.6	+ 7.6
FIVE IRON				
Titleist Tour 100 Balata	166.6	Base	183.8	Base
Example 1 ball	167.1	+ 0.5	182.0	- 1.8
PITCHING WEDGE				
Titleist Tour 100 Balata	102.6	Base	107.9	Base
Example 1 ball	103.0	+ 0.4	106.8	- 1.1

The comparative flight test data indicates that the inventive ball is measurably longer than the Titleist Tour 100 ball off the hard driver at 7, 9, and 11° launch angles. Also, the inventive ball has parity holding with five iron and wedge shots.

Balls formed in accordance with Example 1 (100-compression) were subjected to the standard cut resistance test of Wilson Sporting Goods Co. The cut resistance test is conducted using a True Temper Driving Machine. The test club used is a pitching wedge. Six (6) balls of each type are tested and hit one time each approximately 1/4 inch above the centerline of the ball (random orientation) at standard clubhead velocities. The golf balls are inspected and graded as follows:

FACTOR	DESCRIPTION
10	No visible mark
9	Must search to find mark
8	Visible dent
7	Feel with fingernail - no cut
6	Fingernail inserts - cut
5	Fingernail inserts to core - core not visible
4	Core visible - core not cut
3	Core just cut
2	Core cut deep
1	Core destroyed

The factors of the six (6) golf balls of each type are averaged to obtain an overall factor. The golf balls are evaluated by relative comparison with other golf balls of known cut resistance.

The inventive balls formed in accordance with Example 1 were compared to Titleist Tour 100 balata, Spalding Tour Edition 100 (Soft Ionomer cover), and Ultra (Hard Surlyn cover), the comparative cut resistance data is found in Table 13.

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TABLE 13

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Ball I.D.	Cut Resistance Factor
Titleist Tour 100 balata	4.8
Spalding Tour Edition 100	6.2
Ultra	7.3
Example 1 ball	7.0

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The data presented illustrates that the inventive ball is dramatically improved for cut resistance over the Titleist Tour 100 balata ball, marginally better than the Tour Edition ball, and nearly parity to the hard Surlyn Ultra ball.

20 **Claims**

1. A golf ball comprising a core (11, 17) and a cover (12, 20), the cover comprising an inner layer (13, 21) of a comparatively hard ionomer resin molded over the core and an outer layer (14, 22) of a comparatively soft material molded over the inner layer, in which the inner layer (13, 21) has a flexural modulus within the range of about 965,25 bar to 6894,65 bar (14,000 - 100,000 psi), the outer layer (14,22) comprising material selected from the class consisting of natural balata, synthetic balata, natural rubber, polybutadiene, and polyoctenylene rubber.
2. The golf ball of claim 1 in which the material of the outer layer (14, 22) is a blend of synthetic or natural balata and polybutadiene.
3. The golf ball of claim 1 in which the outer layer (14, 22) is formed from a composition comprising:
 - a) natural or synthetic balata;
 - b) an elastomer which is crosslinkable with a metallic salt of an unsaturated fatty acid;
 - c) a metallic salt of an unsaturated fatty acid as a crosslinking agent; and
 - d) a crosslinking initiator which provides a source of free radicals.
4. The golf ball of claim 3 in which the elastomer of the outer layer (14, 22) is selected from the group consisting of polybutadiene and polyoctenylene.
5. The golf ball of one of the claims 1 to 4 in which the natural or synthetic balata of the outer layer (14, 22) is present in an amount ranging from 25 to 99% of the total weight of polymer of the outer layer and the crosslinkable elastomer is present in an amount ranging from 1 to 75% of the total rate of polymer of the outer layer.
6. The golf ball of claim 3 or 4 in which the crosslinking agent of the outer layer is selected from the group of metallic salts consisting of calcium and magnesium.
7. The golf ball of claim 3 or 4 in which the crosslinking agent of the outer layer is selected from the group of zinc, calcium, and magnesium salts of monocarboxylic acids.
8. The golf ball of claim 3 or 4 in which the crosslinking initiator of the outer layer is organic peroxide.
9. The golf ball of claim 3 or 4 in which the core (11) is a solid core or which the core (17) is a 2 piece core comprising a center (18) and a layer (19) of elastic windings over the center.
10. The golf ball of claim 1 or 3 in which, the outer layer (14, 22) is formed from a composition comprising:
 - a) from 25 to 99 parts by weight of natural or synthetic balata;
 - b) from 1 to 75 parts by weight of an elastomer which is crosslinkable with a metallic salt of an unsaturated fatty

acid; ;

- c) from 20 to 50 parts by weight of a metallic salt of an unsaturated fatty acid as a crosslinking agent; and
- d) from 3/4 to 3-1/2 parts by weight of a crosslinking initiator which provides a source of free radicals.

- 5 11. The golf ball of claim 3, 4 or 10 in which the crosslinkable elastomer of the outer layer is polybutadiene.
12. The golf ball of claim 3, 4, 10 or 11 in which the polybutadiene is cis 1,4 polybutadiene having a cis content of at least 40%.
- 10 13. The golf ball with a diameter of at least 42,67 mm (1.680 inches) of at least one of the claims 1 to 12, in which the diameter of the core (11, 17) is within the range of about 25,40 mm to 38,10 mm (1.000 to 1.500 inch), the thickness of the inner layer (13, 21) is within the range of about 0,635 mm to 7,30 mm (0.0250 to 0.2875 inch), the thickness of the outer layer (14, 22) is within the range of about 1,143 mm to 16,51 mm (0.0450 to 0.650 inch).
- 15 14. The golf ball of claim 13 in which the diameter of the core (11, 17) is about 38,10 mm (1.500 inch), the thickness of the inner layer (13, 21) is about 0,9525 mm (0.0375 inch), the thickness of the outer layer (14, 22) is about 1,3335 mm (0.0525 inch).
- 20 15. A method of making a golf ball comprising the steps of:
- 25 a) forming a spherical core;
- b) molding ionomer resin over the core to form a first cover layer;
- c) forming a blended composition of balata, crosslinkable elastomer, a metallic salt of an unsaturated fatty acid as a crosslinking agent, and a crosslinking initiator which provides a source of free radicals; and
- 25 d) molding said blended composition over the first cover layer to form a second cover layer and to crosslink the crosslinkable elastomer.
- 30 16. The method of claim 15 in which the molding of the blended composition is performed under a temperature of about 121,11°C to 176,67°C (250 to 350°F) for about 5 to 10 minutes.
- 35 17. The method of claim 14 or 15 in which the diameter of the core is formed within the range of about 25,40 mm to 38,10 mm (1.000 to 1.500 inch), the first cover layer is molded to a thickness within the range of about 0,635 mm to 7,30 mm (0.0250 to 0.2875 inch) and the second cover layer is molded to a thickness within the range of about 1,143 mm to 16,51 mm (0.0450 to 0.650 inch).
- 40 18. The method of claim 17 in which the diameter of the core is about 38,10 mm (1.500 inch), the first cover layer is molded to a thickness of about 0,9525 mm (0.0375 inch) and the second cover layer is molded to a thickness of about 1,3335 mm (0.0525 inch).

40 Patentansprüche

1. Golfball mit einem Kern (11, 17) und einer Umhüllung (12, 20), bei dem die Umhüllung eine Innenschicht (13, 21) aus einem über den Kern geformten, relativ harten Ionomer-Harz und eine Außenschicht (14, 22) aus einem über die Innenschicht geformten, relativ weichen Material umfaßt, wobei die Innenschicht (13, 21) ein Biege-Elastizitätsmodul im Bereich von etwa 965,25 bar bis 6894,65 bar (14000 - 100000 psi) aufweist und die Außenschicht (14, 22) ein aus der aus natürlicher Balata, synthetischer Balata, Naturkautschuk, Polybutadien und Polyoctenylen-Gummi bestehenden Klasse gewähltes Material enthält.
2. Golfball nach Anspruch 1, dadurch gekennzeichnet, daß das Material der Außenschicht (14, 22) aus einer Mischung aus synthetischer oder natürlicher Balata und Polybutadien besteht.
- 50 3. Golfball nach Anspruch 1, dadurch gekennzeichnet, daß die Außenschicht (14, 22) aus einer Zusammensetzung gebildet ist, die enthält:
- 55 a) natürliche oder synthetische Balata;
- b) ein Elastomer, das mit einem Metallsalz einer ungesättigten Fettsäure vernetzbar ist;
- c) ein Metallsalz einer ungesättigten Fettsäure als Vernetzungsmittel; und
- d) einen Vernetzungsinitiator, welcher eine Quelle freier Radikale liefert.

4. Golfball nach Anspruch 3, dadurch gekennzeichnet, daß das Elastomer der Außenschicht (14, 22) aus der aus Polybutadien und Polyoctenylen bestehenden Gruppe gewählt ist.
5. Golfball nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die natürliche oder synthetische Balata der Außenschicht (14, 22) in einer Größenordnung von 25 bis 99% des Gesamtgewichts des in der Außenschicht enthaltenen Polymers und das vernetzbare Elastomer in einer Größenordnung von 1 bis 75% des Gesamtgehalts des in der Außenschicht enthaltenen Polymers vorhanden sind.
10. Golfball nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß das Vernetzungsmittel der Außenschicht aus der aus Kalzium und Magnesium bestehenden Gruppe von Metallsalzen gewählt ist.
15. Golfball nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß das Vernetzungsmittel der Außenschicht aus der Gruppe aus Zink, Kalzium und Magnesiumsalzen von Monocarboxylsäuren gewählt ist.
20. Golfball nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß der Vernetzungsinitiator der Außenschicht aus organischem Peroxid besteht.
25. Golfball nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß der Kern (11) aus einem festen Kern besteht bzw. daß der Kern (17) zweiteilig ist und ein Zentrum (18) sowie eine Schicht (19) aus einer elastischen Umwicklung um das Zentrum herum enthält.
30. Golfball nach Anspruch 1 oder 3, bei welchem die Außenschicht (14, 22) aus einer Zusammensetzung gebildet ist, die enthält:
 - a) 25 bis 99 Gewichtsanteile natürlicher oder synthetischer Balata;
 - b) 1 bis 75 Gewichtsanteile Elastomer, welches mit einem Metallsalz einer ungesättigten Fettsäure vernetzbar ist;
 - c) 20 bis 50 Gewichtsanteile eines Metallsalzes einer ungesättigten Fettsäure als Vernetzungsmittel; und
 - d) 3/4 bis 3-1/2 Gewichtsanteile eines Vernetzungsinitiators, welcher eine Quelle freier Radikale liefert.
35. Golfball nach Anspruch 3, 4 oder 10, dadurch gekennzeichnet, daß das vernetzbare Elastomer der Außenschicht aus Polybutadien besteht.
40. Golfball nach Anspruch 3, 4, 10 oder 11, dadurch gekennzeichnet, daß das Polybutadien aus Cis 1,4 Polybutadien mit einem Cis-Gehalt von zumindest 40% besteht.
45. Golfball mit einem Durchmesser von zumindest 42,67 mm (1.680 Inch) nach zumindest einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß der Durchmesser des Kerns (11, 17) im Bereich von etwa 25,40 mm bis 38,10 mm (1.000 bis 1.500 Inch), die Dicke der Innenschicht (13, 21) in einem Bereich von etwa 0,635 mm bis 7,30 mm (0.0250 bis 0.2875 Inch), die Dicke der Außenschicht (14, 22) in einem Bereich von etwa 1,143 mm bis 16,51 mm (0.0450 bis 0.650 Inch) liegen.
50. Golfball nach Anspruch 13, dadurch gekennzeichnet, daß der Durchmesser des Kerns (11, 17) etwa 38,10 mm (1.500 Inch), die Dicke der Innenschicht (13, 21) etwa 0,9525 mm (0.0375 Inch), die Dicke der Außenschicht (14, 22) etwa 1,3335 mm (0.0525 Inch) betragen.
55. Verfahren zur Herstellung eines Golballes mit den folgenden Schritten:
 - a) Formen eines kugelförmigen Kerns;
 - b) Formpressen eines Ionomer-Harzes über den Kern zur Bildung einer ersten Umhüllungsschicht;
 - c) Herstellen einer vermischten Zusammensetzung aus Balata, vernetzbarem Elastomer, einem Metallsalz einer ungesättigten Fettsäure als Vernetzungsmittel und einem Vernetzungsinitiator, welcher eine Quelle freier Radikale liefert; und
 - d) Formen dieser vermischten Zusammensetzung über die erste Hüllschicht zur Bildung einer zweiten Hüllschicht und zum Vernetzen des vernetzbaren Elastomers.
60. Verfahren nach Anspruch 15, dadurch gekennzeichnet, daß das Formen der vermischten Zusammensetzung bei einer Temperatur von etwa 121,11°C bis 176,67°C (250 bis 350°F) während 5 bis 10 Minuten erfolgt.

17. Verfahren nach Anspruch 15 oder 16, dadurch gekennzeichnet, daß der Durchmesser des Kerns im Bereich von 25,40 mm bis 38,10 mm (1.000 bis 1.500 inch), die erste Hüllschicht mit einer Dicke im Bereich von 0,635 mm bis 7,30 mm (0.0250 bis 0.2875 inch) und die zweite Hüllschicht mit einer Dicke im Bereich von 1,143 mm bis 16,51 mm (0.0450 bis 0.650 inch) geformt werden.

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18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß der Durchmesser des Kerns mit etwa 38,10 mm (1.500 inch), die erste Hüllschicht mit einer Dicke von etwa 0,9525 mm (0.0375 inch) sowie die zweite Hüllschicht mit einer Dicke von etwa 1,3335 mm (0.0525 inch) geformt werden.

10 Revendications

1. Une balle de golf comprenant un noyau (11, 17) et une enveloppe (12, 20), l'enveloppe comprenant une couche interne (13, 21) d'une résine ionomère relativement dure moulée sur le noyau et une couche externe (14, 22) d'un matériau relativement mou moulé sur la couche interne, dans laquelle la couche interne (13, 21) présente un module de flexion compris entre environ 965,25 bars et 6894,65 bars (14 000 à 100 000 psi), la couche externe (14, 22) comprenant un matériau choisi parmi la classe consistant en balata naturel, balata synthétique, caoutchouc naturel, polybutadiène et caoutchouc polyocténylène.

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2. La balle de golf selon la revendication 1, dans laquelle le matériau de la couche externe (14, 22) est un mélange de balata synthétique ou naturel et de polybutadiène.

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3. La balle de golf selon la revendication 1, dans laquelle la couche externe (14, 22) est formée d'une composition comprenant :

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- a) du balata naturel ou synthétique ;
- b) un élastomère qui est réticulable avec un sel métallique d'un acide gras insaturé ;
- c) un sel métallique d'un acide gras insaturé en tant qu'agent de réticulation ; et
- d) un initiateur de réticulation qui est une source de radicaux libres.

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4. La balle de golf selon la revendication 3, dans laquelle l'élastomère de la couche externe (14, 22) est choisi dans le groupe consistant en polybutadiène et polyocténylène.

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5. La balle de golf selon l'une des revendications 1 à 4, dans laquelle le balata naturel ou synthétique de la couche externe (14, 22) est présent à raison de 25 à 99 % du poids total de polymère de la couche externe et l'élastomère réticulable est présent à raison de 1 à 75 % de la proportion totale de polymère de la couche externe.

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6. La balle de golf selon la revendication 3 ou 4, dans laquelle l'agent de réticulation de la couche externe est choisi dans le groupe des sels métalliques consistant en calcium et magnésium.

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7. La balle de golf selon la revendication 3 ou 4, dans laquelle l'agent de réticulation de la couche externe est choisi dans le groupe des sels de zinc, de calcium et de magnésium d'acide monocarboxylique.

8. La balle de golf selon la revendication 3 ou 4, dans laquelle l'initiateur de réticulation de la couche externe est un peroxyde organique.

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9. La balle de golf selon la revendication 3 ou 4, dans laquelle le noyau (11) est un noyau plein ou bien dans laquelle le noyau (17) est un noyau en deux parties comprenant un centre (18) et une couche (19) d'enroulements élastiques sur le centre.

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10. La balle de golf selon la revendication 1 ou 3, dans laquelle la couche externe (14, 22) est constituée d'une composition comprenant :

- a) de 25 à 99 parties en poids de balata naturel ou synthétique ;
- b) de 1 à 75 parties en poids d'un élastomère qui est réticulable avec un sel métallique d'un acide gras insaturé ;
- c) de 20 à 50 parties en poids d'un sel métallique d'un acide gras insaturé en tant qu'agent de réticulation ; et
- d) 3/4 à 3-1/2 parties en poids d'un initiateur de réticulation qui constitue une source de radicaux libres.

11. La balle de golf selon la revendication 3, 4 ou 10, dans laquelle l'élastomère réticulable de la couche externe est

du polybutadiène.

12. La balle de golf selon la revendication 3, 4, 10 ou 11, dans laquelle le polybutadiène est du cis 1,4-polybutadiène ayant une teneur en cis d'au moins 40 %.
- 5 13. La balle de golf d'un diamètre d'au moins 42,67 mm (1,680 pouce) selon au moins l'une des revendications 1 à 12, dans laquelle le diamètre du noyau (11, 17) est compris entre environ 25,4 mm et 38,10 mm (1,000 à 1,500 pouce), l'épaisseur de la couche interne (13, 21) est comprise entre environ 0,635 mm et 7,30 mm (0,0250 et 0,2875 pouce), l'épaisseur de la couche externe (14, 22) est comprise entre environ 1,143 mm et 16,51 min (0,0450 à 10 0,650 pouce).
14. La balle de golf selon la revendication 13, dans laquelle le diamètre du noyau (11, 17) est d'environ 38,10 mm (1,500 pouce), l'épaisseur de la couche interne (13, 21) est d'environ 0,9525 mm (0,0375 pouce), l'épaisseur de la couche externe (14, 22) est d'environ 1,3335 mm (0,0525 pouce).
- 15 15. Un procédé de fabrication d'une balle de golf comprenant les opérations de :
 - a) formation d'un noyau sphérique ;
 - b) moulage d'une résine ionomère sur le noyau pour former une première couche de couverture ;
 - c) formation d'une composition mélangée de balata, d'élastomère réticulable, d'un sel métallique d'un acide gras insaturé en tant qu'agent de réticulation, et d'un initiateur de réticulation qui constitue une source de radicaux libres ; et
 - d) moulage de ladite composition mélangée sur la première couche de couverture pour former une seconde couche de couverture et pour réticuler l'élastomère réticulable.
- 25 16. Le procédé selon la revendication 15, dans lequel le moulage de la composition mélangée est réalisé à une température d'environ 121,11°C à 176,67°C (250 à 350°F) pendant environ 5 à 10 minutes.
17. Le procédé selon la revendication 14 ou 15, dans lequel le noyau est formé avec un diamètre compris dans la 30 gamme entre environ 25,40 mm à 38,10 mm (1 à 1,5 pouce), la première couche de couverture est moulée à une épaisseur comprise dans la gamme d'environ 0,635 mm à 7,30 mm (0,0250 à 0,2870 pouces) et la deuxième couche de couverture est moulée à une épaisseur comprise dans la gamme d'environ 1,153 mm à 16,51 mm (0,0450 à 0,65 pouce).
- 35 18. Le procédé selon la revendication 17, dans lequel le diamètre du noyau est d'environ 38,10 mm (1,5 pouce), la première couche de couverture est moulée à une épaisseur d'environ 0,9525 mm (0,0375 pouce) et la deuxième couche de couverture est moulée à une épaisseur d'environ 1,3325 mm (0,0525 pouce).

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Fig. 1

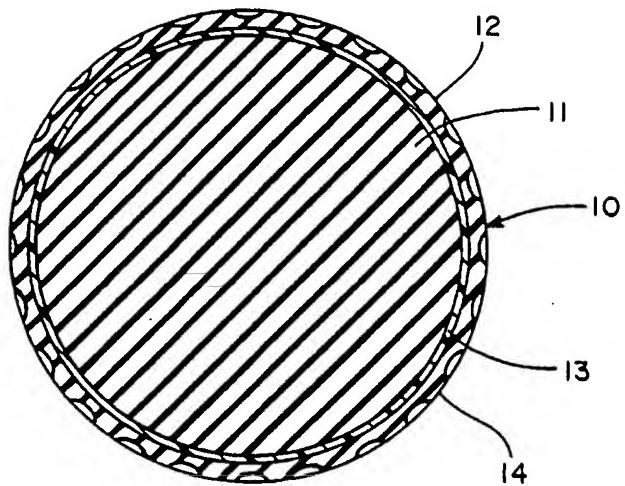


Fig. 2

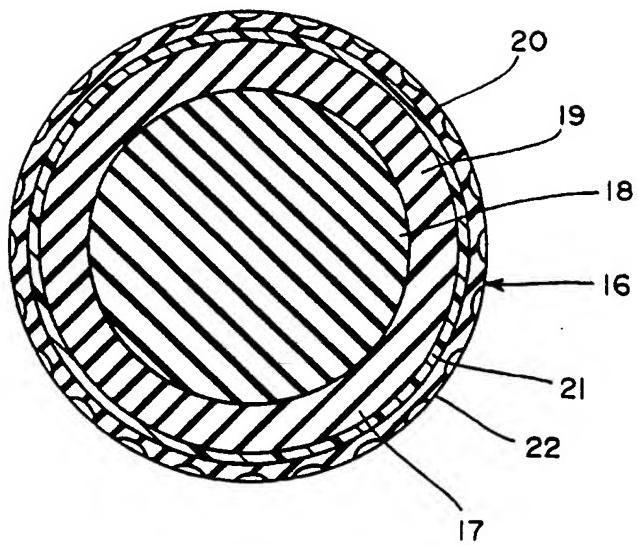


Fig. 3

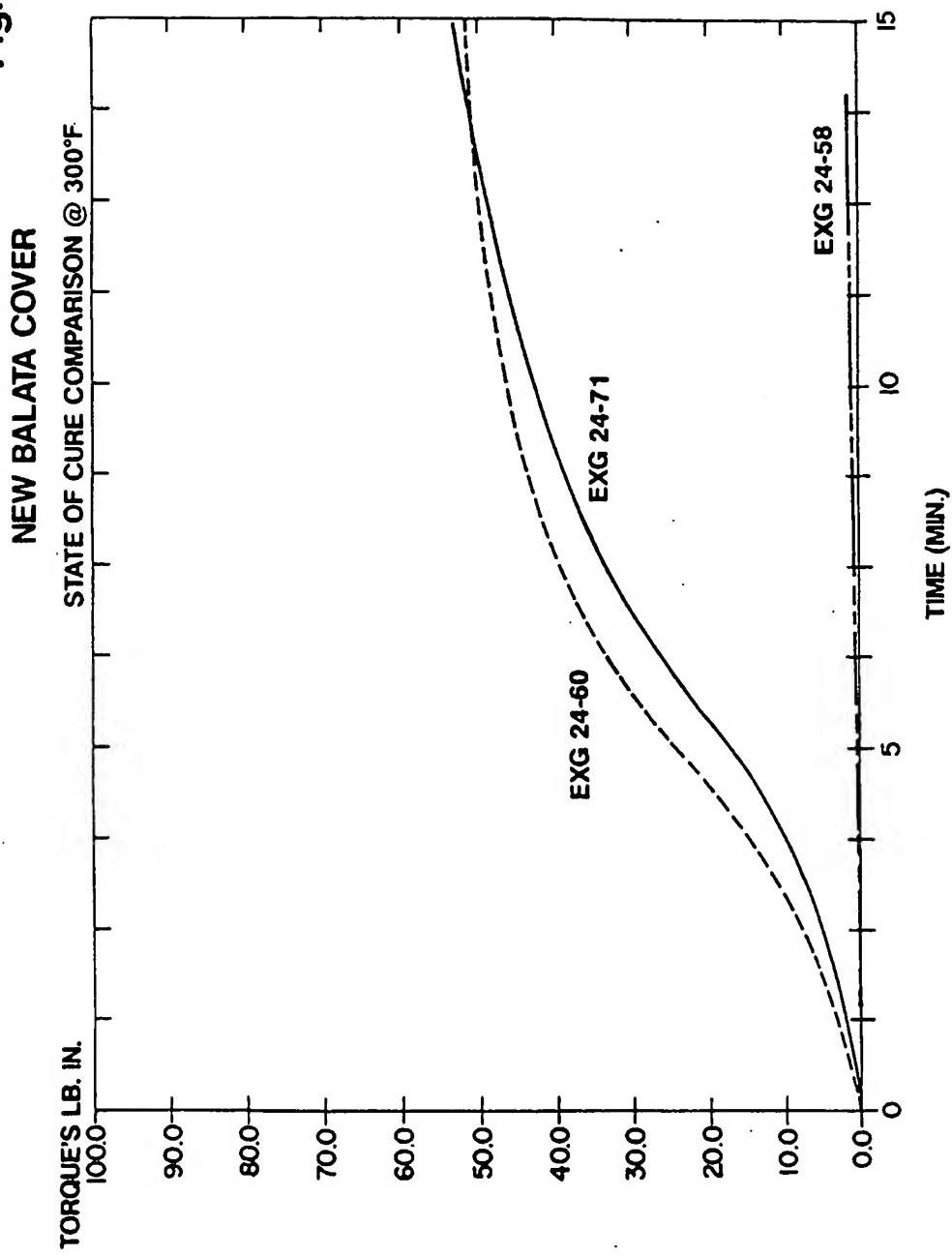


Fig. 4

